Lead, atomic absorption spectrometric, graphite furnace

Parameter and Code:
Lead, dissolved, I-1401-85 (µg/L as Pb): 01049

1. Application

1.1 This method may be used to determine lead in low ionic-strength water and precipitation. With deuterium background correction and a 20-µL sample, the method is applicable in the range from 0.3 to 20 µg/L. With Zeeman background correction and a 20-µL sample, the method is applicable in the range from 0.5 to 50 µg/L. Sample solutions that contain lead concentrations exceeding the upper limits must be diluted or preferably be analyzed by the atomic absorption spectrometric direct or chelation extraction method, or by the atomic emission spectrometric ICP method.

1.2 The analytical range and detection limits can be increased or possibly decreased by varying the volume of sample injected or the instrumental settings. Purification of reagents and use of ASTM Type 1 water (Method D-1193, American Society for Testing and Materials, 1984) may result in lower detection limits.

2. Summary of method

Lead is determined by atomic absorption spectrometry in conjunction with a graphite furnace containing a graphite platform (Hinderberger and others, 1981). A sample is placed on the graphite platform and a matrix modifier is added. The sample is then evaporated to dryness, charred, and atomized using high-temperature ramping. The absorption signal generated during atomization is recorded and compared with standards.

3. Interferences

3.1 Interferences in low ionic-strength samples, such as precipitation, normally are quite low. In addition, the use of the graphite platform reduces the effects of many interferences. Calcium (25 mg/L), magnesium (8 mg/L), sodium (20 mg/L), sulfate (34 mg/L), and chloride (25 mg/L) do not interfere. Higher concentrations of these constituents were not investigated.

3.2 Precipitation samples usually contain very low concentrations of lead. Special precautionary measures must be employed during both sample collection and laboratory determination to prevent contribution from contamination.

4. Apparatus

4.1 *Atomic absorption spectrometer,* for use at 283.3 nm and equipped with background correction, digital integrator to quantitate peak areas, graphite furnace with temperature programmer, and automatic sample injector. The programmer must have high-temperature ramping and stopped-flow capabilities.

4.1.1 Refer to the manufacturer's manual to optimize instrumental performance. The analytical ranges reported in paragraph 1.1 are for a 20-µL sample with 5 µL of matrix modifier (NOTE 1).

NOTE 1. A 20-µL sample generally requires 30 s to dry. Samples that have a complex matrix may require a longer drying and charring time.

4.1.2 *Graphite furnace,* capable of reaching temperatures sufficient to atomize the element of interest. **Warning**: dial settings frequently are inaccurate and newly conditioned furnaces require temperature calibration.

4.1.3 *Graphite tubes and platforms.* Pyrolytically coated graphite tubes and solid pyrolytic graphite platforms are recommended.

4.2 *Labware.* Many trace metals at very low concentrations have been found to sorb very rapidly to glassware. To preclude this,

fluorinated ethylene propylene (FEP) or Teflon labware may be used. Alternately, glassware, particularly flasks and pipets, may be treated with silicone anti-wetting agent such as Surfacil (Pierce Chemical Co., Rockford, IL, 61105) according to the manufacturer's instructions. Autosampler cups must be checked for contamination. Lancer (1831 Olive St., St. Louis, MO, 63103) polystyrene disposable cups have been found to be satisfactory after acid rinsing. Alternately, reuseable Teflon or FEP cups may be used.

4.3 *Argon,* standard, welder's grade, commercially available. Nitrogen may also be used if recommended by the instrument manufacturer.

5. Reagents

5.1 *Lead standard solution I,* 1.00 mL = 1,000 µg Pb: Dissolve 1.0000 g Pb shot in a minimum of dilute HNO_3. Heat to increase rate of dissolution. Add 10 mL high-purity, concentrated HNO_3 (sp gr 1.41) Ultrex or equivalent and dilute to 1,000 mL with Type 1 water.

5.2 *Lead standard solution II,* 1.00 mL = 10.0 µg Pb: Dilute 10.0 mL lead standard solution I to 1,000 mL (NOTE 2).

NOTE 2. Use acidified Type 1 water (paragraph 5.7) to make dilutions. All standards must be stored in sealed Teflon or FEP containers. Each container must be rinsed twice with a small volume of standard before being filled. Standards stored for 6 months in FEP containers yielded values equal to those of freshly prepared standards.

5.3 *Lead standard solution III,* 1.00 mL = 1.00 µg Pb: Dilute 100.0 mL lead standard solution II to 1,000 mL. This standard is used to prepare working standards serially at time of analysis.

5.4 *Lead standard solution IV,* 1.00 mL = 0.010 µg Pb: Dilute 10.0 mL lead standard solution III to 1,000 mL. This standard also is used to prepare working standards serially at time of analysis.

5.5 *Matrix modifier solution,* 40 g $NH_4H_2PO_4$/L: Add 40.0 g $NH_4H_2PO_4$ to 950 mL Type 1 water, mix, and dilute to 1,000 mL. Analyze 20 µL of matrix modifier for lead contamination. If the lead reading is more than 0.005 absorbance-seconds, purify the solution by chelation with ammonium pyrrolidine dithiocarbamate (APDC) and extraction with methyl isobutyl ketone (MIBK) (NOTE 3). Analyze 20 µL of the purified solution. Repeat extractions until the lead level is reduced to the acceptable level. **DO NOT ADD ACID TO THE PURI-FIED MATRIX MODIFIER SOLUTION.**

NOTE 3. To purify matrix modifier solution, pour the solution into a Teflon or FEP container. Add 0.25g APDC for each liter of solution. While stirring, adjust the solution to pH 2.9 by dropwise addition of concentrated HNO_3 (sp gr 1.41). Transfer portions of the solution to a separatory funnel, add 100 mL MIBK/liter of solution, and shake vigorously for at least 5 min. Frequently, vent the funnel in a hood. Collect the extracted solution in the FEP container. Repeat the extraction with 50 mL MIBK/liter of solution. Because MIBK can dissolve some plastic autosampler cups, boil the solution for at least 10 min in a silicone-treated or acid-rinsed container covered with a watchglass to remove MIBK.

5.6 *Nitric acid concentrated,* high-purity, (sp gr 1.41): J. T. Baker "Ultrex" brand HNO_3 has been found to be adequately pure; however, each lot must be checked for contamination. Analyze acidified Type 1 water for lead. Add an additional 1.5 mL of concentrated HNO_3/liter of water, and repeat analysis. The integrated signal should not increase by more than 0.003 absorbance-seconds.

5.7 *Water, acidified,* Type 1: Add 1.5 mL high-purity, concentrated HNO_3 (sp gr 1.41) to each liter of water.

5.8 *Water, Type 1.*

6. Procedure

6.1 Systematically clean and rinse work areas with deionized water on a regular schedule. Use a laminar flow hood or a "clean room" environment during sample transfers. Ideally, the autosampler and the graphite furnace should be in a clean environment.

6.2 Soak autosampler cups at least overnight in a 1 + 1 solution of Type 1 water and high-purity nitric acid.

6.3 Rinse the sample cups twice with sample before filling. Place cups in sample tray and cover. Adjust sampler so that only the injection tip contacts the sample.

6.4 In sequence, inject 20-µL aliquots of blank and working standards plus 5 µL of modifier each and analyze. Analyze the blank and working standards twice. Construct the analytical curve from the integrated peak areas (absorbance-seconds). Generally, the curve should be linear to a peak-absorbance (peak-height) value of 0.40 absorbance units.

6.5 Similarly, inject and analyze the samples twice. Every tenth sample cup should contain either a standard or a reference material.

6.6 Restandardize as required. Minor changes of values for known samples usually indicate deterioration of the furnace tube, contact rings, and (or) platform. A major variation usually indicates either autosampler malfunction or residue buildup from a complex matrix in a previous sample.

7. Calculations

Determine the micrograms per liter of lead in each sample from the digital display or printer output. Dilute those samples containing concentrations of lead that exceed the working range of the method; repeat the analysis, and multiply by the proper dilution factors.

8. Report

Report lead, dissolved (01049), concentrations as follows: less than 10.0 µg/L, nearest 0.1 µg/L; 10 µg/L and above, two significant figures for both deuterium background correction and Zeeman background correction.

9. Precision

9.1 Analysis of six samples six times each by a single operator using deuterium background correction is as follows:

Mean (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)
1.13	0.13	12
2.06	0.12	5.7
3.95	0.16	4.1
6.02	0.22	3.6
10.41	0.32	3.1
20.21	0.35	1.7

9.2 Analysis of five samples by a single operator using Zeeman background correction is as follows:

Number of Replicates	Mean (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)
4	0.62	0.17	27
4	1.80	0.27	15
4	5.68	0.05	0.9
10	24.00	0.77	3.2
14	48.31	0.79	1.6

9.3 The precision and bias for the Zeeman background correction were tested on deionized water and tap water (specific conductance 280 µS/cm). A known amount of lead was added to each sample, and single-operator precision and bias for six replicates are as follows:

Amount added (µg/L)	Amount found (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Recovery (percent)
Deionized water				
11	10.63	0.48	4.5	97
13.5	13.30	0.78	5.9	98
15	15.27	0.96	6.3	102
22	21.40	0.58	2.7	97
30	29.37	0.54	1.8	98
Tap water (NOTE 4)				
11	10.15	1.19	10	92
13.5	15.37	2.40	15	114
15	15.18	0.92	5.6	101
22	20.88	0.83	3.7	95
30	30.81	1.70	5.3	103

NOTE 4. The tap water contained 1.3 µg/L of lead, and the standard deviation and percent relative standard deviation were calculated prior to subtraction of lead originally present.

9.4 The precision and bias for the deuterium background method were tested on deionized water and tap water (specific conductance 280 µS/cm). A known amount of lead was added to each sample, and single-operator precision and bias for six replicates are as follows:

Amount added (µg/L)	Amount found (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Recovery (percent)
Deionized water				
11	10.70	0.81	7.6	97
13.5	12.63	1.18	9.3	94
15	13.82	0.76	5.5	92
22	21.18	0.86	4.1	96
30	30.60	1.72	5.6	102
Tap water (NOTE 4)				
11	10.64	0.63	5.3	97
13.5	15.37	1.59	9.9	114
15	17.78	3.70	19.4	119
22	21.49	1.97	8.6	98
30	29.68	1.13	3.7	99

9.5 Interlaboratory precision for dissolved lead for 16 samples within the range of 3.4 to 37.4 µg/L, without regard to type of background correction and use of matrix modifiers, if any, may be expressed as follows:

$$S_T = 0.448X + 1.478$$

where

S_T = overall precision, micrograms per liter, and

X = concentration of lead, micrograms per liter.

The correlation coefficient is 0.8247.

References

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